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CANADIAN PATENT

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**METHOD OF PRODUCING SHAPED HYDRATED CALCIUM
SILICATE PRODUCTS**

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**Granted to Johns-Manville Corporation,
U. S. A.**

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METHOD OF PRODUCING SHAPED
HYDRATED CALCIUM SILICATE PRODUCTS

Background of the Invention

Field of the Invention

This invention relates to a method for the production of shaped articles formed from calcium silicate slurries.

Shaped calcium silicate products are widely used, particularly as insulation materials. These products are commonly formed by combining a source of calcium oxide, such as lime, with a siliceous material, such as sand, in the presence of water. On heating this mixture in an autoclave, a variety of crystalline forms of calcium silicate may be formed, depending upon the temperature, pressure, length of reaction time, and water concentration used. Fibrous materials, such as asbestos, which are not adversely affected by the reaction conditions may be incorporated into the mixture prior to processing. The reaction product of this processing is generally an aqueous slurry of hydrated calcium silicate crystals with which will be intermixed any fibrous components present. This slurry is cast into molds and is dried, usually by the application of heat, to form the desired finished shaped objects.

The processing to form the crystalline materials in the slurry is usually quite time-consuming and requires large and expensive pieces of processing equipment. Much effort, therefore, is directed toward improving the process conditions under which crystallization takes place and also shortening the period of time required to produce a finished hydrate. A desirable improvement would be one which permitted a reduction in the size of processing equipment while maintaining the same or increased

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1 throughput, which would reduce the capital investment required to perform the process. Further, improved processes which lessen the amount of time required to take the slurry from ambient conditions, through the crystallization step, and return to ambient conditions, would result both in more efficient and economical utilization of the equipment and also in an increased output of finished product. Consequently, a process which will accomplish all of the objects would be highly desirable.

10 In addition, such an improved process should seek to overcome particular processing problems found in prior art processes. One serious problem occurs upon completion of crystallization when one seeks to reduce the pressure within the autoclave and cool the slurry to return it to ambient conditions. Simply allowing the steam pressure to be reduced by cooling is very slow and inefficient, for the heat transfer from the hot aqueous slurry through the thick autoclave walls to the atmosphere is very slow. Consequently, it has been the practice of operators in the past to vent the steam pressure to the atmosphere. Since the crystallization reaction normally proceeds at temperatures well above the boiling point of water under atmospheric pressure, this sudden release of steam pressure causes the hot aqueous slurry to boil violently. This violent boiling, in turn, fractures many of the newly formed crystals, thus defeating much of the prior careful crystallization processing. Further, the venting of steam to the atmosphere is quite wasteful of heat energy.

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Description of the Prior Art

A wide variety of crystalline forms of hydrated calcium silicate are described by Taylor, J. of Appl. Chem.,

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1 10, 317 (Aug., 1960). Numerous patents disclose the hydrothermal formation of the various calcium silicate hydrates; representative examples include U. S. Reissue Patent 19,005 and U. S. Patents 2,215,891; 2,665,996; 2,699,097; 3,116,158 and 3,501,324. U. S. Patents 2,665,996 and 3,501,324 also describe incorporation of fibrous reinforcements, such as asbestos or cellulose, into the slurry of initial reactants prior to the hydrothermal crystallization step.

10 Summary

It has not been discovered that the advantages of reduced processing time, less costly and massive processing equipment, better product formation, and more efficient processing can be obtained by the process of this invention. In this process, a highly concentrated aqueous slurry of a source of calcium oxide and a siliceous material is hydrothermally reacted in the presence of saturated steam under elevated pressure in a pressure vessel to form crystalline calcium silicate. Following formation of the desired crystalline calcium silicate hydrate, the steam input is halted and low temperature water is gradually added to the reaction mixture within the pressure vessel until sufficient water has been added to dilute the crystalline slurry to the desired degree of concentration for subsequent molding operations. The incoming water condenses the steam in the pressure vessel, simultaneously reducing the pressure within the vessel and cooling the crystal-containing slurry. The gradual cooling and depressurization effectively eliminates disruption of the crystal structure formed. In addition, the period of time required to raise the reaction mixture from ambient conditions to crystallization reaction

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1 conditions is substantially reduced, for the amount of
water present which must be heated is significantly less
than in the prior art processes.

Detailed Description of the Invention

10 The process of this invention permits the
efficient formation of shaped calcium silicate hydrate
articles which may, if desired, contain fibrous reinforce-
ment. Processing equipment can be utilized in a more
efficient manner than could the equipment for operating
prior art processes, in that overall reaction times can
be substantially reduced, which in turn permits increased
production rates. Further, since the volume of material
handled under high pressure conditions is significantly
less than that handled in prior art processes, the volume
of the reaction vessels and consequently their mass can
also be significantly reduced, thus leading to a sub-
stantial reduction in capital investment.

20 In addition to the substantial processing
advantages, higher quality products may also be obtained
by the process of this invention. The process of this
invention eliminates the step required in previous pro-
cesses in which high pressure steam was vented to the
atmosphere at the end of the crystallization reaction
to reduce the pressure within the pressure vessel. This
abrupt reduction of pressure caused violent boiling in
the aqueous mass of crystals, which in turn caused serious
disruption and fracturing of the newly formed crystals.
The process of this invention permits a gradual decrease
in pressure within the pressure vessel and so avoids damag-
ing turbulence in the crystal containing slurry.

30 These advantages are accomplished by the pro-
cess of this invention, which is a process for forming

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1 shaped hydrated calcium silicate objects and which comprises: a) forming a concentrated aqueous slurry of a siliceous material and a source of calcium oxide, b) heating the concentrated slurry in a pressure vessel in the presence of saturated steam at a pressure of at least 75 psig for a period of at least one-half hour to form the desired calcium silicate hydrate crystalline forms, c) thereafter gradually adding water to the slurry in the pressure vessel to dilute the crystal-containing slurry and to simultaneously gradually reduce the temperature and pressure within the pressure vessel to approximately ambient pressure and a temperature below 212°F, d) removing the diluted slurry from the pressure vessel, and e) forming it into the desired shape after which it is dried to obtain the shaped objects. If desired, fibrous reinforcement may also be incorporated into the composition either before the hydrothermal formation of crystals or following crystallization but prior to molding.

20 The hydrothermal crystallization step of this invention is conducted in a suitable pressure vessel (which normally is a conventional autoclave) with provision for agitating the slurry. The concentrated slurry containing the source of calcium oxide and the siliceous material, as well as any desired fibrous reinforcement which will not be degraded under the hydrothermal conditions, is placed in the autoclave and heated by high pressure saturated steam. The steam pressure is generally within the range of from 75 to 500 psig, preferably 100-250 psig; the temperature will be that of the saturated steam at the particular pressure (thus over this particular pressure range, the temperature

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1 will range from about 321°F. to about 470°F). The parti-
cular pressure and associated temperature which are used
will be determined by the predominant type of calcium
silicate hydrate crystal which is desired. The time of
reaction at the operating temperature will also be de-
termined by the type of crystal form of the calcium
silicate hydrate desired. Normally, the reaction time
will be between 0.5 and 20 hours, preferably 2-8 hours.
The particular hydrothermal reaction conditions which
10 favor the formation of one crystalline type over another
are amply described in the art. For instance, U. S.
Patent 2,665,996 describes the different conditions which
favor respectively the formation of a calcium silicate
hydrate with the formula $4\text{CaO} \cdot 5\text{SiO}_2 \cdot 5\text{H}_2\text{O}$ or a calcium
silicate hydrate with the formula $5\text{CaO} \cdot 5\text{SiO}_2 \cdot \text{H}_2\text{O}$. The
patent also mentions other conditions which may lead to
the formation of gyrolite, calcium silicate hydrate II,
hillebrandite, and/or calcium silicate hydrate I. Simi-
larly, U. S. Patent 3,501,324 describes the conditions
20 which lead respectively to tobermorite and xonotlite.

The slurry which contains the source of calcium
oxide and the siliceous material (and perhaps fibrous
reinforcement) will have a water:solids weight in
range of from 3:1 to 8:1, preferably 4:1 to 6.5:1. This
material is referred to herein as the "concentrated
slurry." Normally the amount of water present will be
no more than that sufficient to permit an adequate dis-
persion of the solid materials and to permit proper
growth of the crystals during the hydrothermal reaction.
30 It is a principal feature of this invention that the
process does not involve the heating under pressure of
any water other than that needed in order to permit

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1 proper crystal growth.

During the crystallization step, the concentrated slurry will be agitated or stirred at least part of the time. It is preferred that the agitation be moderate and constant during the crystallization step although if desired, periodic agitation can be used. In the latter case, it is preferred that the agitation be during the early portion of the crystallization step, and followed by a period of quiescence. Agitation may
10 be by any conventional means, such as paddles, bladed mixers, and the like. The degree of agitation should be such that thorough mixing of the reactants is obtained but crystal formation is not substantially impeded. Operation of conventional agitating devices in an optimum manner under these conditions is well within the skill of those versed in the art of mixing and need not be further detailed here.

Following completion of the crystallization step, the supply of saturated steam to the pressure vessel is stopped. The phrase "completion of the crystalli-
20 zation step" are used herein refers to that point at which essentially all of the desired quantity of the desired type of crystals have been obtained in the slurry. It is recognized that crystal growth does not halt instantly and that some crystal growth will continue during the cooling and water addition phase of the process. However, the amount of crystals so formed does not represent a significant addition to the crystals already present and therefore, for practical purposes, crystalli-
30 zation can be considered to have been completed at the time the steam is shut off and the water addition begun.

The water addition is accomplished by any

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1 convenient means. Normally this will be by a piping
arrangement which permits gradual addition of cool water
to the hot concentrated aqueous slurry. Alternatively
or additionally, water can be introduced into the pres-
sure vessel by means of spraying devices within the
pressure vessel. In any event, introduction of the
water materially cools and dilutes the concentrated
slurry, while simultaneously reducing the internal pres-
sure in the vessel by condensing the steam. The rate
10 of water introduction is regulated to maintain the
maximum rate which can be attained without serious dis-
ruption of the crystal mass. In general, this means
that the water introduction rate will be such that at
any given period of time the temperature of the water
in the slurry will be less than the boiling temperature
of water at the pressure then present in the vessel.
To accomplish this, it is normally required that there
be some direct cooling of the slurry itself, as by water
addition directly into the slurry, rather than complete
20 reliance upon spray condensation of the steam in the
vessel. The techniques for accomplishing this controlled
cooldown by water introduction are well known and are
readily within the abilities of those skilled in the art
of operating processes which involve the use of saturated
steam. A preferred method is to introduce the water in
small amounts at spaced intervals of time. For instance,
the total amount of water could be added in five equal
increments of one minute's addition each spaced apart by
ten minute intervals.

30 The pressure in the pressure vessel will be
reduced by the water addition to approximately ambient
pressure. "Approximately ambient pressure" as used

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1 herein means a pressure not exceeding 50 psig, but preferably not exceeding 40 psig. It has been found that when the pressure in the pressure vessel is below this level, the remaining steam may be safely vented to the atmosphere with little disruption of the crystalline mass and a minimum loss of heat energy. Further, venting the remaining steam to the atmosphere once this pressure range has been reached permits significant shortening of the process cycle without serious adverse affects on the quality of the product obtained.

10 The water:solids weight ratio of the diluted slurry which is taken from the pressure vessel following water addition and cooling will be about 8:1 to 25:1, preferably 12:1 to 20:1. The particular concentration will be that most amenable to the specific molding and drying steps which follow. Thus, a greater degree of dilution enhances the flow properties of the calcium silicate hydrate mass, particularly if fibrous reinforcement is present. In addition, the degree of dilution obtained will be to some extent dependent upon the amount of pressure reduction and cooling required in the preceding step, as well as being in part a function of the temperature of the incoming water.

20 Following dilution of the concentrated slurry and attendant temperature and pressure reduction, the diluted slurry is removed from the pressure vessel and formed into the desired finished product, usually by molding and drying. If desired, fibrous reinforcement may be added prior to molding. Such reinforcement may be in addition to any fibrous reinforcement present in the initial slurry prior to crystallization or it may constitute the only fibrous reinforcement in the material.

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1 Fibrous materials which may advantageously be added
following removal of the dilute slurry from the pressure
vessel are those which would be adversely affected by
the temperature and pressure conditions in the vessel.
The dilute slurry of calcium silicate hydrate and any
fibrous reinforcement can be molded readily into any
desired shape by the conventional shaping processes such
as compression molding, extrusion molding, casting,
shaping with filter press or wet machine, etc. The
10 molded slurry may be dried simply by allowing the slurry
to stand under ambient conditions. Alternatively, the
slurry may be heated in a drying atmosphere if faster
drying is desired.

 The source of calcium oxide of the invention
may be any of the common calcareous materials such as
quicklime, slaked lime, acetylene residuum, carbide
residuum, etc. The siliceous material may include a
natural or synthetic amorphous silica or silicate or
mixtures thereof. Typical examples include quartz,
20 silica flour, siliceous sand, diatomaceous earth, clays,
silica gel, etc. Small amounts of other compounds in
addition to silica may be present in the siliceous ma-
terial, such as alumina, and in fact may be advantageous
in the formation of particular crystalline forms of
calcium silicate hydrate. The mole ratio of calcium
oxide:silica will generally range from about 0.5:1 to
3.0:1 depending upon the particular crystalline hydrate
desired. The mole ratio will preferably be in the range
of approximately 0.75:1 to 2.0:1.

80 The fibrous reinforcement may be inorganic or
organic fibrous materials. The inorganic materials will
include asbestos fibers, rockwool, and glass fibers. The

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1 organic materials will include natural cellulosic fibers
and synthetic fibrous materials such as rayons and nylons.
Fibrous materials which are not adversely affected by
the reaction conditions in the pressure vessels may be
added either before or after the crystallization reaction.
Those which are deteriorated by such conditions will be
added following the crystallization reactions.

The shaped products of the process of this in-
vention may be used directly as obtained following the
drying step. They may also, if desired, be coated,
10 painted or otherwise further prepared for their ultimate
uses.

The following example will illustrate the pro-
cess of this invention. To 137 gallons of water heated
in a premixer to 200°F. were added 95 pounds of powdered
quartz and 95 pounds of hydrated lime. These were
thoroughly blended to form a concentrated slurry having
a water:solids weight ratio of 5.5:1. The concentrated
slurry was charged to a preheated reactor which was
20 equipped with a variable speed bladed stirrer. The
reactor was charged with steam to a pressure of 165
psig; this pressure was maintained for four hours with
constant stirring of the slurry by the mixer rotating
at 20 rpm. At the end of the four hours, the steam
supply was shut off and cool water introduced at the
rate of 40 gallons per minute for five one minute inter-
vals, each separated by a ten minute interval; the total
water addition was therefore 200 gallons. When the pres-
sure was reduced to 35 psig, the pressure vessel was
30 exhausted to the atmosphere. The diluted slurry was
then ready for removal from the pressure vessel and
formation into molded, dried shaped objects.

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1 In another example, the crystalline calcium silicate hydrate was formed as described in the preceding paragraph. Following removal of the diluted crystalline slurry from the pressure vessel, six pounds of 1/8 inch glass fiber and four pounds of 3/8 inch 1.5 denier rayon fibers were mixed directly into the diluted slurry and thoroughly dispersed. The fiber reinforced material was then ready for molding and drying.

10 The fiber reinforced products of this invention normally have average densities in the range of 11.5 to 14.5 lbs/ft³, moduli of rupture (dry) on the order of 100 psi, and compressive strength (dry) on the order of 180 psi. Thermal conductivity at 700°F. mean temperature is on the order of 0.7 BTU-in/hr-ft²-°F. These values compare favorably with, and in some cases exceed, the corresponding values for asbestos fiber reinforced calcium silicate materials formed by prior art processes. The process of this invention, therefore, is capable of producing satisfactory (in some cases superior) 20 calcium silicate materials for insulation and other uses while yet avoiding many of the disadvantages of the prior art processes. Most notably, the length of the overall processing cycle can be substantially reduced by the process of this invention with no adverse affect upon the product quality.

20 The above description details the invention and sets forth illustrative examples of materials and embodiments of the invention. It will be immediately apparent to those skilled in the art, or will become so upon practice of the invention, that there are numerous 30 other embodiments clearly within the scope and spirit of this invention. Consequently, the scope of the

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1 invention is to be determined solely from the appended claims.

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